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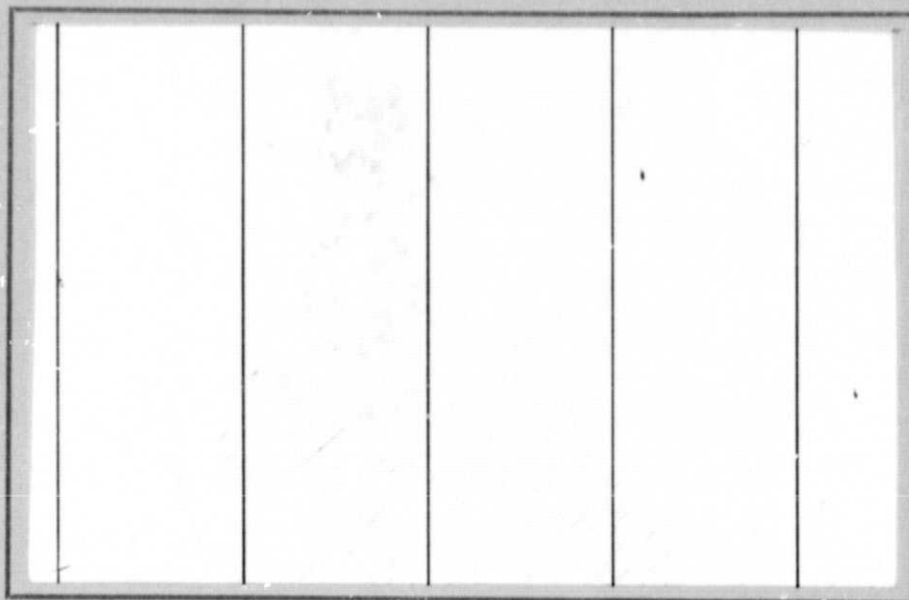
NSG-1124

(NASA-CR-148312) EFFECT OF POLYMER
PROPERTIES AND ADHESION SURFACES ON ADHESION
Semiannual Report (Virginia Polytechnic
Inst. and State Univ.) 20 p HC \$3.50

N76-27425

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CSCI 11G G3/27



Virginia Polytechnic Institute
and State University

Chemistry Department
Blacksburg, Virginia 24061



SEMI-ANNUAL REPORT

EFFECT OF POLYMER PROPERTIES AND
ADHEREND SURFACES ON ADHESION

by

David W. Dwight and James P. Wightman

Prepared for

National Aeronautics and Space Administration

July, 1976

Grant NSG-1124

NASA-Langley Research Center
Hampton, Virginia 23665
Materials Division
Donald J. Progar

Department of Chemistry
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

I. INTRODUCTION

Earlier work emphasized synthesis and strength-testing of novel high-temperature polymers, including variations in solvent, amine and anhydride in the adhesive formulation; aluminum, titanium and composite adherends; high-temperature aging and strength-testing; and aluminum powder adhesive filler (1). We evaluated the surface characteristics associated with joint strength, using ESCA, SEM/EDAX, SRIRS and contact angles in a variety of preliminary experiments (2).

Based upon those results, SEM/EDAX stood out as most effective. Detailed analysis of the surface structures of fractured joints revealed unique characteristics typical of specific adhesive formulations and test conditions. A "fracture mechanics" model was developed to promote correlations between macroscopic shear strength and the microstructure of fracture surfaces. Applications were made to unpublished data on polyimides and fluoropolymers. The basic soundness of this semi-empirical approach to improved adhesive-bonding was tested through three contributions to the scientific literature (3) and several invited lectures in a unique series of international meetings on surface science (3). We have thus refined our method and have established a useful approach to understanding the microscopic basis of adhesive strength (or weakness) via detailed analysis of fracture surfaces. Technological innovations of interest to NASA-LaRC can now be analyzed quickly, with confidence in a predictive model for adhesive behavior.

SEM analyses were performed on selected samples representing various combined effects of composite adherends, high-temperature testing, aluminum filler and fiber glass "carrier cloth." Preliminary experiments to cast films from polyamic acids for ESCA and contact-angle measurements re-emphasized the problem of bubbling during attempts to prepare heat-imidized films. Thermogravimetric analysis (TGA) identified the major volatile product as residual solvent (rather than water of imidization), and attempts were made to define conditions of time, temperature and vacuum that would produce bubble-free films.

Poor utility of the AEI ES-100 ESCA apparatus prevented collection of spectra during the grant period, but careful study of current literature established the utility and importance of quantitative aspects (4) and of shake-up phenomena in ESCA analysis of polymers.

II. DISCUSSION

A. Fracture Mechanics Model: Theory and Experiment

Our qualitative survey of the "fracture mechanics" approach to strength-of-materials identified (1) inherent flaws, (2) viscoelastic and plastic deformation, (3) crazing and crack propagation, and (4) interfacial failure as the main factors contributing to overall joint strength. Examples of the appearance of each of these mechanisms were illustrated by reference to new fracture-surface studies in

fluoropolymers and polyimides (3). The general conclusion was that mechanisms (1) and (4) decreased strength, while (2) and (3) increased strength. (Purely elastic contributions to strength may be significant and would be undetectable in static SEM; thus rheological measurements--WLF, rate-temperature superposition--are necessary to estimate the contribution of bulk polymer properties to strength.) Unique fracture surfaces were shown to result from changes in polymer structure, surface treatments, solvent, amine, anhydride, filler, adherend, and test temperature. Trends in strength results were correlated with the proportion of mechanisms (1)-(4) operating, as estimated by usual examination of micrographs and adherends.

A unique sequence of international meetings on surface science afforded the opportunity to present these results directly to the leading authorities in the field. We found positive response, typified by Prof. J. J. Bikerman, "on the whole, your views are in gratifying agreement with mine (5)." Two other experts in the field, R. J. Good and A. N. Gent are now beginning to concentrate their efforts in SEM examination of fracture surfaces (6). Thus we have confidence in our semi-empirical approach toward understanding the microscopic phenomena associated with adhesive strength.

For systems of specific interest to NASA-LaRC, we concluded that voids of random size and location were generated by residual solvent (or perhaps water-of-imidization) during cure, and they were the main cause for poor reproducibility

and lowered shear strengths; they limited the area for polymer deformation and were nucleation sites for fracture. The preimidized film adhesive was the exception, pointing the way for future development: no voids and good strength inspite of interfacial failure.

The frustrating complexity of the interplay of variables emerged from fractography vs adhesive formulation. Solvents DG and DMF gave good interfacial contact, but DG promoted plastic deformation while DMF gave high-area brittle fracture. The interface looked weak with DMAC, correlating with little deformation, fracture area or strength. Anhydride PMDA or para-structures in the amine appeared more brittle than BTDA, ODPa or m-amine polymers, and also showed more interfacial failure.

Strength and micro-mechanics of fracture were virtually unchanged by prolonged, high -temperature aging, but voids and interfacial failure increased when the test-temperature increased, and strength dropped. A combination of flow under stress at high temperature and weakened interfacial forces due to differential thermal expansion appeared to decrease strength. Interfacial failure was eliminated and an order-of-magnitude reduction in the size of fracture-surface features were induced by aluminum powder adhesive filler; high-temperature strength doubled. EDAX measurements established that fracture propagated farther from the interface at high temperatures. Pl3N-composite adherends

apparently take up much of the volatiles released in the adhesive during cure, and fracture occurs predominantly in the composite surface.

The preceding observations and interpretations have served as valuable guidelines for a new generation of high-performance adhesive systems now under development at NASA-LaRC. The interdisciplinary program has thus established a sound, scientific basis in both synthesis and analysis, and can proceed confidently with technological objectives.

B. Recent Results

High-strength fiber composites are of special interest in advanced aerospace technology, and we have studied several samples that encompass most of the typical process and test variables (Table 1). The complexity of interacting variables is magnified by a variety of adherend parameters that did not enter the picture with titanium substrates: the components and methods of preparation of composite substrates appear to be a major factor determining shear strength. Moreover, these joints are very sensitive to distribution of flaws and stresses during bonding and of strains during shear testing. When failure occurs within the composite a characteristic brittle failure propagates along a tortuous path through the polymer matrix and along polymer/fiber interfaces. Polymer failure has no plastic component, the brittle fracture surfaces have no louvering, and polymer-fiber bonds apparently have been broken. However, for the

set of composites fabricated from Pl3N polyimide at NASA-LaRC, strength almost doubled the values obtained with Skybond 710 composites prepared by General Dynamics. Close examination reveals a sharper, more brittle appearance of the matrix fracture and more fine "explosive" debris with Pl3N. In this case strength did not vary significantly when the locus of failure shifted into the composite surface (when higher pressure was used to mold the composite). On the other hand, when fracture propagated in the adhesive layer, strength increased 50% when Skybond 710 composite substrates were employed. During the latter experiments it appeared that the geometry of stressing the specimen during strength testing may be an important variable: In two of three comparisons, the use of a spacer in the Instron grips produced 50-100% decrease in strength, while shifting the locus of failure from the adhesive layer into the composite surface. Moreover, while cutting samples for mounting on SEM stubs, the composites delaminated easily under perpendicular pressure from the cutting bar, i.e., strength between layers in these composites is less than the strength within a given ply. Thus, if the test geometry is such as to maximize stress between plies in the composite and initiate cracks there, then the substrate will delaminate and the overall joint strength will be low.

The use of fiber glass "carrier cloth" is an expedient in the preparation of adhesive bonds with polyimides. However, the introduction of this new variable contributed to

poor reproducibility. Fractography on the anomalously low-strength samples indicated that the mechanical response of the joint was changed by the cloth layer, as well as the potential for stress concentrations and nucleation sites. At high temperature, fracture occurs in an apparently weak region of adhesive between the carrier cloth and substrate: a myriad of small voids with some plastically deformed walls and a small area of ductile-type fracture characterize the topography. Without the carrier cloth, the voids are absent, deformation and fracture areas increase dramatically, and almost half the fracture occurs within the composite surface (without loss of strength). Removal of the aluminum powder filler halves the strength; fractography shows larger features - voids, plastic deformation and brittle fracture - but the overall area of the latter two strength-producing mechanisms decreases by one or two orders of magnitude. At room temperature, the "neat" polyimide adhesive has large voids and some fracture in the composite surface. High-area brittle fracture in the void-cell walls, plus the overall (fortuitously optimal) geometry of joint and test must together be responsible for the excellent strength.

Also photomicrographs were taken of Alcan MD-105 aluminum powder used as 63% by weight filler in the LARC-3 formulation. These fine, rounded particles have a size range of about 1-25 μ , their surfaces have a rough, "thatched" microstructure, and correspond to the lumps observed in LARC-3, as expected. Increased EDAX aluminum intensities for a

group of particles compared with the LARC-3 fracture surface, clearly shows the attenuating effects of overlying polymer.

C. Polymer Properties

One result of fracture mechanics theory has not been tested experimentally in our program: rheological contributions, in principle, can be estimated by the Williams-Landau-Ferry (WLF) superposition principle applied to strength-vs-rate and temperature data. Also we need uniform, reproducible polymer films for theoretically promising experiments to elucidate polymer-surface structure and bonding via ESCA and contact-angle hysteresis. The problems encountered in attempts to prepare films are unresolved, and too many uncontrolled variables remain when any other than the thinnest films are cast. For example, we noted that the polyamic acids (BDTA + 3,3'- or 4,4'-DABP) are yellow when cast from diglyme and clear when cast from DMAC. One can imagine chromophores generated due to peroxides, but wouldn't expect a significant effect upon strength, so we have not pursued it further than a series of SRIRS experiments that were not definitive.

More troublesome was uncontrollable void formation, despite a variety of time, temperature and vacuum conditions during the cure cycle. Several considerations point to residual solvent rather than water-of-imidization as the principal source of void formation. First, rough calculation

based on solids content and stoichiometry of imidization shows that the volume of solvent liberated from 15% solutions exceeds the water of imidization by at least an order of magnitude. Second, the solvents are high-boiling, low vapor pressure materials and the polymers are glassy. Third, no practicable conditions could be found to eliminate the onset of voids in the vicinity of the solvent boiling point. Figure 1 shows the thermogravimetric analysis of a film cast by eight brushings on fiber glass carrier cloth, left standing three weeks and finally left under vacuum overnight at 100°C. Clearly the principal weight loss still occurs at the boiling point of diglyme (163°C), and virtually no weight loss occurs between 250-400°C, where one would expect to detect water of imidization.

D. ESCA

This technique was used extensively during earlier work to obtain chemical structure and bonding data primarily on metallic adherends, before and after various surface-preparation steps. Severe operating problems plagued the ESCA equipment during the current grant period, and even instruction in operation of the instrument was postponed, to say nothing of obtaining useful spectra. Therefore we restricted our efforts to gedanken study of optimizing the information content in ESCA experiments and correctly analyzing and interpreting the results.

Primary consideration was given to the quantitative aspects of ESCA peak intensities in terms of stoichiometry of the surface region. This is most important and controversial area in electron spectroscopy currently, and leading authorities hold divergent opinions in some cases. Literature review and discussions with experts identified a number of factors that must be taken into account when interpreting ESCA intensity ratios (complications of interpreting absolute intensities eliminate practical utility today). Table 2 outlines roughly what the experimentalist must consider before attempting even semi-quantitative surface analysis.

Briefly, inorganic samples present greater difficulty than organic samples in general, although the latter class suffers more from x-ray beam damage and limited range of binding energy and chemical shift information. Other factors are minimized by comparing intensities of photoelectrons with very similar kinetic energy. Sample roughness and instrumental beam geometry have been shown experimentally to alter even relative intensity ratios in ESCA. The effect has been predicted theoretically, and thus ratios may be corrected by accurate knowledge of the respective geometrical factors. Either assumptions must be made or independent experimental evidence invoked to take both lateral and in-depth distribution of elements in the specific sample matrix into account.

Intensity of primary ESCA peaks is diminished by interaction of the photoelectron with the matrix. "Extrinsic"

processes such as inelastic scattering, phonon excitation, etc. and "intrinsic" mechanisms such as shake-up and shake-off phenomena must be considered explicitly. This means that the entire photoelectron spectrum must be recorded and all significant peaks included in calculations of relative atomic composition of the sampled volume. These computations require knowledge of the relative sensitivity or cross-section for photoionization for each peak; tables of values have been published, but there is a disturbing lack of agreement in some cases. Hydrocarbons deposit on the sample surface during most practical ESCA measurements; correction for contamination must be made.

Fortunately there are a variety of ways to obtain corroborative information to facilitate quantitative applications of ESCA, although the experimental time required may increase intolerably. The use of measurements on standards and model compounds, combined with theoretical calculations based on chemical and physical structure models, is the classical analytical approach. In situ cleaning (or depth-profiling) by ion beams or plasmas can remove contamination and other surface layers. Data on the spacial distribution of elements within the sampled volume can be obtained from variation in take-off angle ("grazing-angle" ESCA), and by using intensity ratios from two photoelectrons ejected from different core levels of the same element.

Recently it has been demonstrated by D. T. Clark and coworkers that analysis of "shake-up satellites" in the ESCA spectra of polymers allows new insight into the structure and bonding at the surface. Although they have shown the most pronounced effects occur in chains with pendant ring structures, the current literature suggests that we should study the satellite region in the ESCA spectra of polymers of interest to NASA-LaRC. Unfortunately, satellite peaks are one or two orders of magnitude less intense (and a few volts lower kinetic energy) than the main peak, and experimental time must increase correspondingly.

III. Future Work

The following program items are a natural extension of several areas of study reported above.

First priority is the SEM/EDAX characterization of new adhesives and substrates under study at NASA-LaRC, aiming to provide guidance by rapid feed-back on the detailed failure mechanisms responsible for the observed strength values. More extensive SEM fractography is required to refine our semi-empirical approach to the science of adhesive bonding.

The methods of Quantitative Stereology must be applied to the photomicrographs to make more precise assessment of the proportions of the constituent strength mechanisms operating in each specimen.

Further exploration of EDAX estimates of surface-layer thickness should be pursued. Calibration standards employing organic and inorganic films of known thickness must be studied vs a number of variables of the SEM (e.g. beam voltage and diameter).

We must obtain qualification to operate the SEM personally in order to accomplish these objectives effectively.

Fracture mechanics theory indicates that useful strength usually involves significant rheological contributions. SEM fractography of NASA-LaRC systems has shown a variety of manifestations of polymer rheology in a sort of "hindsight" fashion. We can measure the rheological contribution in principle by collecting data on strength vs. both temperature and rate of testing. But this requires a many series of samples made identically and without voids.

Lower priority experiments still promise to yield useful information about conformation, structure and bonding in the surface region of the polymers of interest to NASA-LaRC. Quantitative and shake-up structure analysis of ESCA spectra were mentioned above, and we plan to supplement those data with measurement of contact-angle hysteresis. Finally, we are considering ways of promoting chemical reactions with surface functional groups to "derivitize" samples for more detailed analysis by ESCA.

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Table 1

<u>NASA- LaRC #</u>	<u>Adhesive</u>	<u>Adherends (1)</u>	<u>Test Temp. °F</u>	<u>Lap Shear Strength (psi)</u>	<u>Locus of Failure Visual and/or SEM</u>
946-D1 (2)	LARC-3	P13N composites molded at 400 psi at NASA- LaRC	25	3400	95% cohesive, high-area brittle fracture of very small void cell walls
947-D1 (2)	LARC-3	P13N composites molded at 1000 psi at NASA- LaRC	25	3700	70/30 composite/cohesive "explod- ing" brittle failure in matrix, sharp fracture edges, scattered debris; fiber surfaces exposed.
948-D1 (2)	LARC-3	P13N composite molded at 400 psi and Ti6-4	25	3800	95% composite, larger voids next to titanium
948-D3 (2)	LARC-3	P13N composite molded at 1000 psi and Ti6-4	25	3900	95% composite, larger voids next to titanium
1044-1	LARC-3	Skybond 710 composites molded at 100 psi at General Dynamics	25	2400 ⁽³⁾	100% composite, fiber surfaces exposed, no plastic deformation, rounded failure edges, no scat- tered debris
1044-2 (2)	LARC-3	Skybond 710 composites molded at 100 psi at General Dynamics	500	2400	60/40 cohesive/composite, very fine, highly drawn adhesive features
1044-4	LARC-3	Skybond 710 composites molded at 100 psi at General Dynamics	75	2200	100% composite fiber surfaces exposed, no plastic deformation rounded failure edges no scat- tered debris
1045-1	LARC-3 + carrier cloth	Skybond 710 composites molded at 100 psi at General Dynamics	25	2300 ⁽³⁾	80/20 composite/cohesive

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Table 1 (continued)

NASA-LaRC #	Adhesive	Adherends (1)	Test Temp. °F	Lap Shear Strength (psi)	Locus of Failure Visual and/or SEM
1045-2(2)	LARC-3 + carrier cloth	Skybond 710 composites molded at 100 psi at General Dynamics	500	600	100% cohesive, many microvoids, some drawing, small fracture area
1045-4	LARC-3 + carrier cloth	Skybond 710 composites molded at 100 psi at General Dynamics	25	1100	70/30 carrier/composite
1046-1(2)	LARC-3(4)	Skybond 710 composites molded at 100 psi at General Dynamics	25	3300(3)	80/20 cohesive/composite large void areas, some drawing, high area brittle fracture
1046-2(2)	LARC-3(4)	Skybond 710 composites molded at 100 psi at General Dynamics	500	1300	70/30 cohesive/composite considerable void area, large plastic deformation, "splintering" fracture
1046-4(2)	LARC-3(4)	Skybond 710 composites molded at 100 psi at General Dynamics	25	2200	95% composite

(1) HT-S graphite fiber/polyimide

(2) SEM/EDAX fractography

(3) No grip spacer used in strength testing

(4) Without 63% aluminum powder filler

TABLE 2

FACTORS INFLUENCING RELATIVE ESCA INTENSITIES

<u>TYPE OF SAMPLE</u>	<u>OTHER PARAMETERS</u>
1. ORGANIC	1. CONTAMINATION
2. INORGANIC	2. LINE SENSITIVITIES
3. SMOOTH FILM	3. MATRIX EFFECTS
4. ROUGH SOLID, FIBER, FABRIC AND PARTICLE	A. ENERGY LOSS B. SCATTERING
5. DISTRIBUTION, 2D & 3D	